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# Reconstruction of the clean and metal-adsorbed Ge(111) surface

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The ion-bombardment-cleaned Ge(111) surface has been observed to undergo $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction prior to the $(2\times8)$ reconstruction. This $(\sqrt{3}\times\sqrt{3})$ surface structure is also observed upon adsorption of Li and Ag. By comparing the measured low-energy electron-diffraction *I-V* curves of the clean surface $(\sqrt{3}\times\sqrt{3})$ reconstructed structure with those of $(\sqrt{3}\times\sqrt{3})$ structures of the Li- and Ag-adsorbed surfaces, it is concluded that all $(\sqrt{3}\times\sqrt{3})$ structures result from surface reconstruction. In addition, a $(1\times3)$ structure on the Ge(111) surface has been also observed as a result of the adsorption of Li, Na, and K. The equivalence of the *I-V* curves for the three $(1\times3)$ structures indicates that germanium surface reconstruction is responsible for the $(1\times3)$ structure. The coverage dependence of the alkali-metal-induced reconstructions is identified.

## I. INTRODUCTION

Surface reconstruction of germanium was first observed many years ago.[1] It is clear now that the clean Ge(111) has reconstructed structures of the $2\times1$, $c(2\times8)$, and incommensurate $(2\times2)$ at different temperatures.[2–5] Recently, however, a $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction of the clean Si(111) surface has been observed by low-energy electron diffraction (LEED).[6] It has been reported there that the ion-bombarded Si(111) surface undergoes a $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction during annealing. Since germanium has the same bulk structure and somewhat similar behavior as silicon, we expected the existence of a $(\sqrt{3}\times\sqrt{3})$ reconstruction on the Ge(111) surface. This curiosity initiated the work to be reported in this paper.

Moreover, many adsorption experiments have been done on semiconductor surfaces, especially on silicon surfaces, and a variety of superstructures have been observed.[7–9] However, it is surprising that *I-V* curves of superstructures generated by different adsorbates are often almost identical. For example, the *I-V* curves of the $(\sqrt{3}\times\sqrt{3})$ phases for clean Si(111) (Ref. 6) and Ta and Ag on Si(111) (Ref. 10) are similar. Such superstructures are due to adsorbate-driven substrate reconstruction and it is also of interest to pursue the question of adsorbate-induced reconstruction in the case of germanium.

In this paper we report the first observation of the $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction of the clean Ge(111) surface, the Ag- and Li-induced $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction of the Ge(111) surface, and other Ge(111) surface reconstructions induced by alkali-metal adsorbates.

## II. EXPERIMENT

The experimental conditions are similar to those described previously.[11] The experimental apparatus consists of an ultrahigh-vacuum (UHV) chamber equipped with a four-grid LEED optics and a video camera interfaced to a personal computer for automated LEED *I-V* curve measurements. The sample was a piece of *p*-type–doped Ge(111) wafer with resistivity of 30 Ω cm. The alkali-metal deposition sources were Saes getter thermal cells mounted about 12 cm away from the sample. The silver source was a piece of tungsten wire with a silver bead at the center. The deposition rates of the sources were calibrated by a quartz microbalance attached next to the sample. The vacuum condition for the experiments was maintained at better than $3\times10^{-10}$ Torr.

## III. RESULTS AND DISCUSSION

### A. $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction of the clean Ge(111) surface

After the germanium sample was mounted into the UHV chamber, the surface was cleaned with several cycles of 1-keV $Ar^+$-ion bombardment and annealed at 700 °C until no impurities were observed in the Auger-electron-spectroscopy (AES) spectrum. The Ge(111) surface was then intensely bombarded by the 1-keV ion beam so that the surface was completely disordered. This disordered surface underwent a disorder-order transition upon annealing to about 500 °C. As shown in Figs. 1(a) and 1(b), the ordered surface has a reconstructed superstructure of $(\sqrt{3}\times\sqrt{3})R30°$ phase after a flash anneal (10 °C/sec) to 500 °C for a few seconds and rapid cooling (20 °C/sec). This $(\sqrt{3}\times\sqrt{3})$ reconstruction has also been observed on the Si(111) surface after a similar surface treatment[6] and is possibly a general feature of the (111) surfaces of diamond-structure crystals.

This $(\sqrt{3}\times\sqrt{3})$ reconstruction of the clean Ge(111) surface was very stable at room temperature and was not due to surface contamination, as there was no indication of impurities in the AES spectra. However, it disappeared after an additional 10-sec anneal at 500 °C and was replaced by a diffuse $(2\times8)$ pattern after cooling, as shown in Fig. 1(c).

The atomic structure of the $(\sqrt{3}\times\sqrt{3})$ reconstruction of the clean Ge(111) surface may be similar to that of the

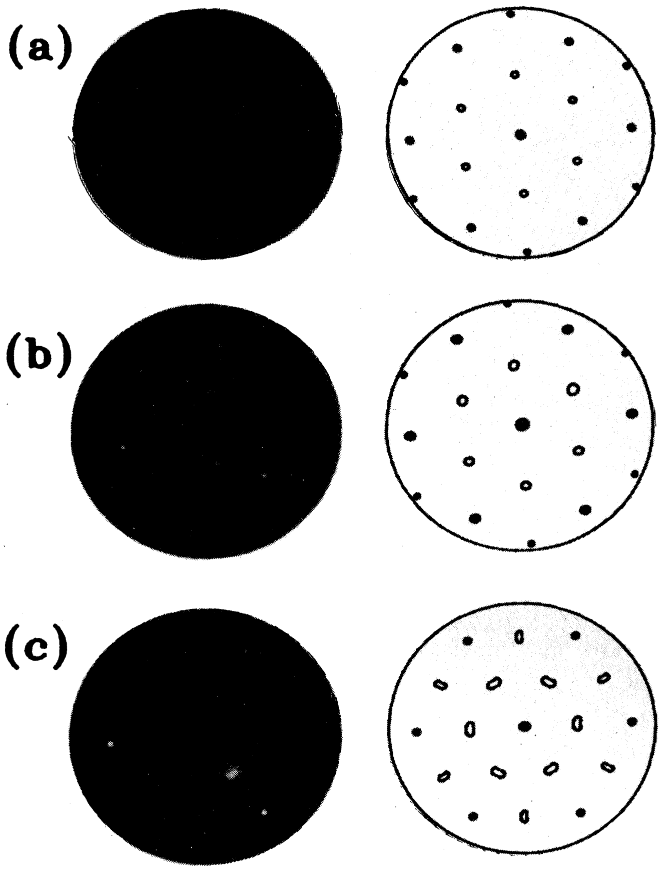

FIG. 1. LEED patterns of the clean Ge(111) surface and their schematic representations. The $(\sqrt{3}\times\sqrt{3})R30^\circ$ reconstruction after annealing at about 500 °C: (a) for 2 sec and (b) for 5 sec. The diffuse $(2\times8)$ reconstruction, (c), after annealing at 500 °C for 5 min.

Si(111) surface.[6] Full dynamical LEED calculations are currently under way to more fully identify the atomic structure.

### B. Alkali metals on the Ge(111) surface

A clean Ge(111) surface with $(2\times8)$ structure was exposed at room temperature to the alkali-metal vapor. The exposure rate was controlled at about 0.1 ML/min [here 1 monolayer (ML) $=7.8\times10^{14}$ atoms/cm$^2$]. The adsorption of alkali metal on the room-temperature substrate did not product any superstructure phase and only enhanced the diffuse background in the diffraction pattern of the $(2\times8)$ phase. As a result, the alkali-metal atoms were probably uniformly distributed and disordered on the surface at room temperature.

However, after the alkali-metal-exposed surface was annealed to about 300 °C for a few seconds, a series of ordered phases were observed at various coverages. Figure 2 shows the observed relationship of the ordered phase with increasing exposure of alkali metals under sequential steps of adsorption and annealing to 300 °C.

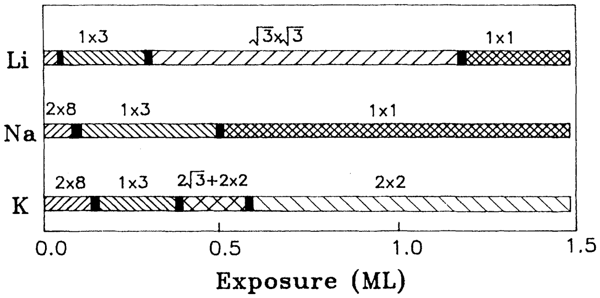

FIG. 2. Relationship of the ordered phases of the Ge(111) surface as a function of the exposure of alkali metals. Each phase is defined after room-temperature exposure and a short 300-°C anneal in vacuum.

At very low exposure, the LEED pattern was modified by increased diffuse background after the anneal at 300 °C. As exposure increased for Li, Na, and K, the diffuse $(2\times8)$ pattern gradually disappeared and was followed by the appearance of a $(1\times3)$ ordered phase after anneal (Fig. 2). This $(1\times3)$ phase has been also observed for alkali-metal adsorption on Si(111).[7] Later in this paper we will confirm that these $(1\times3)$ structures are due to substrate reconstruction instead of the ordering of the adsorbates.

Further increases in the exposure of the alkali metals resulted in a variety of superstructures dependent upon the alkali-metal specie. For Li adsorption, a $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure was observed after an exposure of about $\frac{1}{3}$ ML and a 300-°C anneal. This $(\sqrt{3}\times\sqrt{3})$ structure slowly disappeared after more than 1 ML Li was evaporated onto the surface followed by the anneal to 300 °C. For sodium adsorption, the $(1\times3)$ structure disappeared at about 0.5 ML exposure, and no superstructure was observed for Na exposure $>0.5$ ML. For potassium adsorption, a $(2\sqrt{3}\times2\sqrt{3})R30^\circ$ structure was

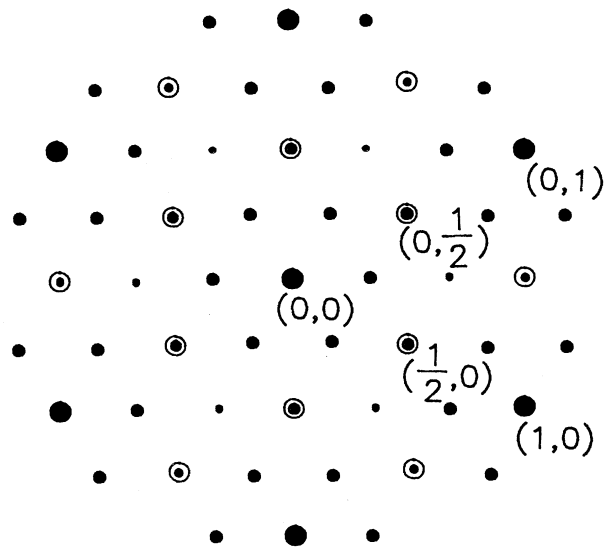

FIG. 3. Schematic LEED pattern of the coexistence of the $(2\sqrt{3}\times2\sqrt{3})R30^\circ$ and $(2\times2)$ phases.

observed soon after the disappearance of the (1×3) structure at a K exposure of about 0.4 ML. With increasing K exposure followed by the 300-°C anneal, the intensities of the half-integer-order diffraction beams increased and the intensities of the other noninteger beams in the $(2\sqrt{3}\times2\sqrt{3})$ phase almost remained unchanged, as shown in Fig. 3. It is clear that the increase in intensities of the half-order beam is an indication of the (2×2) ordering in the K adsorbate. The diffraction pattern (Fig. 3) eventually represented coexistence of the $(2\sqrt{3}\times2\sqrt{3})$ and the (2×2) phases. This coexistence converted to a diffuse (2×2) phase after the K exposure reached about 0.6 ML. The (2×2) phase became more and more diffuse and very slowly disappeared with further increase of the exposure followed by the 300-°C anneal.

### C. Ag on the Ge(111) surface

A $(\sqrt{3}\times\sqrt{3})R30°$ structure was produced after the Ge(111) surface was exposed to about 0.5 ML silver and

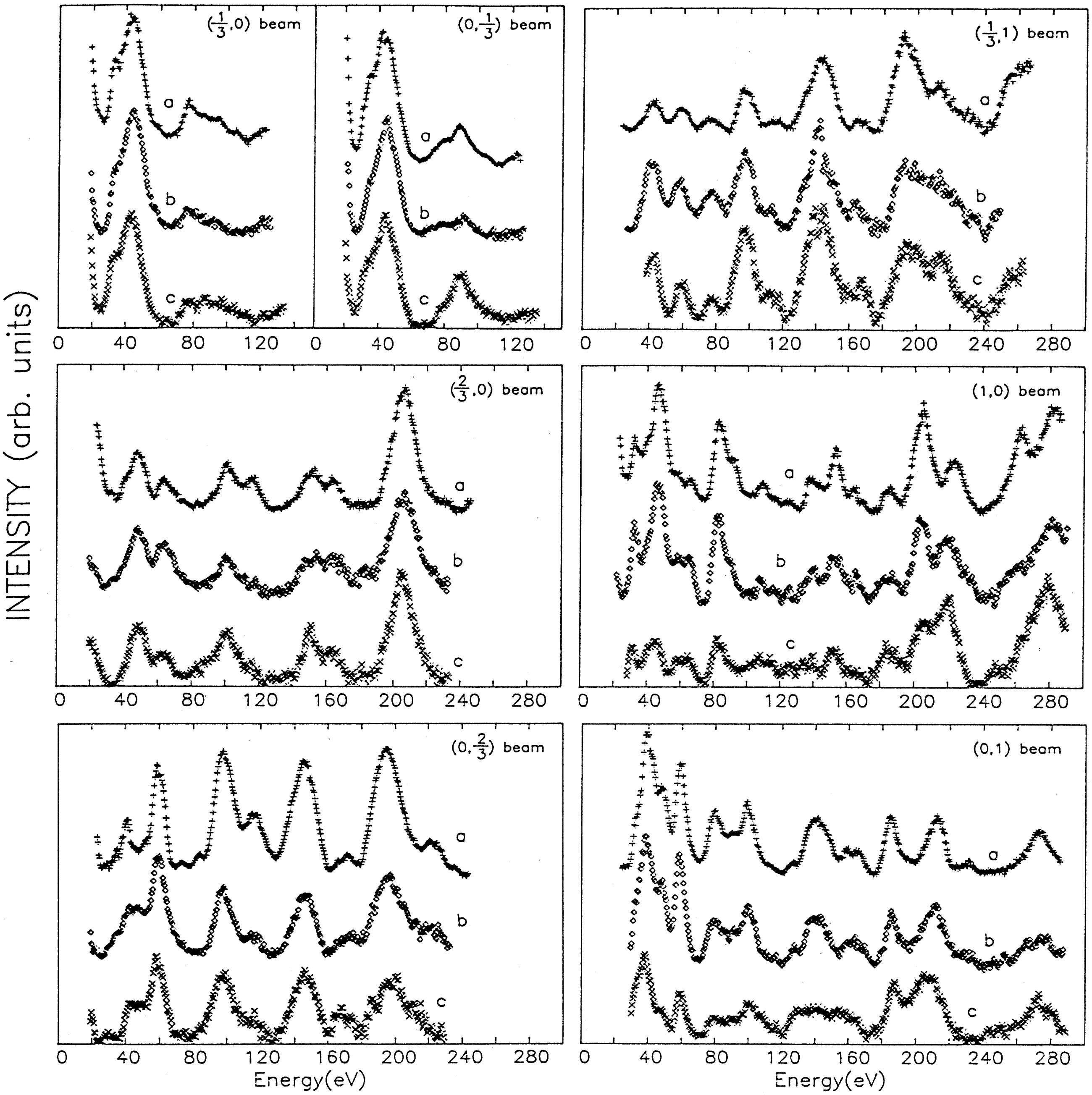

FIG. 4. *I-V* curves for the (1×3) structures observed for the Ge(111) surface upon adsorption of (a) Li, (b) Na, and (c) K, all at an exposure of 0.3 ML and a short anneal at 300 °C.

annealed to about 400 °C for several minutes. The *I-V* curves for the $(\sqrt{3}\times\sqrt{3})$ structure were measured at room temperature for comparison to the clean Ge(111) $(\sqrt{3}\times\sqrt{3})$ *I-V* curves. This $(\sqrt{3}\times\sqrt{3})$ phase of Ag on the Ge(111) surface was first observed two decades ago.[9] The relationship between this $(\sqrt{3}\times\sqrt{3})$ phase and other ordered phases of Ag on the Ge(111) has been also described in the literature[8] as a function of coverage and temperature.

### D. Discussion of measured *I-V* curves

LEED intensity-energy spectra (*I-V* curves) are very sensitive to surface atomic structures and have been used to determine the surface atomic structures for more than two decades.[12,13] A straightforward structural consideration based on the LEED curves is the following: If two sets of measured *I-V* curves of the same phase for the same substrate but for different adsorbates are equivalent to each other, they then have to represent the same surface atomic structure, e.g., surface reconstruction. Therefore, *I-V* curves from similar superstructure phases for different adsorbates can be used for the direct determination of whether the adsorbates form a simple overlayer structure, or induce substrate reconstruction.

Figure 4 shows measured *I-V* curves for the $(1\times3)$ superstructures of alkali metals on the Ge(111) surface at the experimental conditions mentioned above. The seven beam sets show consistent similarities between each curve in a set. Within most of the energy range used, the *I-V* curves of each set are virtually identical to one another, in spite of the variation of the alkali-metal adsorbate specie used. These similarities in the *I-V* curves clearly indicate that the $(1\times3)$ superstructure generated by alkali-metal adsorption is a result of the substrate reconstruction rather than ordering in the alkali-metal overlayers. The adsorption of alkali metals on the Ge(111) surface could clearly change the Ge-Ge interatomic potential, i.e., modify features of the chemical bonds in the germanium surface, inducing a reconstruction to the $(1\times3)$ structure for which the total energy could be lower and thus the structure more stable than the $(2\times8)$ reconstruction.

The $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction of the clean Ge(111) surface is analogous to the observed $(\sqrt{3}\times\sqrt{3})$ reconstruction of the clean Si(111) surface.[6] It has also been pointed out in Ref. 6 that the $(\sqrt{3}\times\sqrt{3})$ structure of Ag on the Si(111) surface is due to the same surface reconstruction, because the *I-V* curves of the $(\sqrt{3}\times\sqrt{3})$

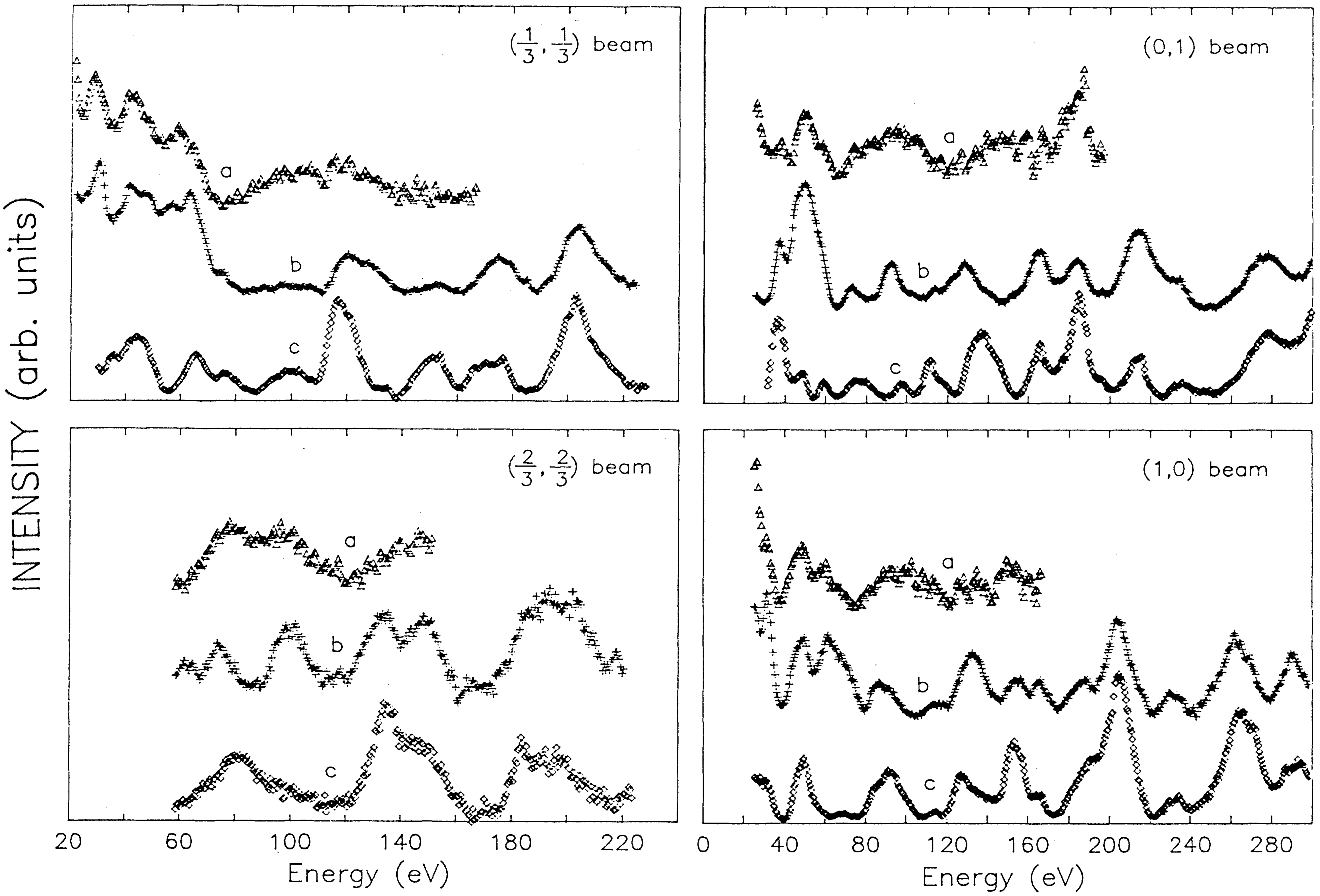

FIG. 5. *I-V* curves for the $(\sqrt{3}\times\sqrt{3})R30°$ structure observed for the Ge(111) surface: (a) clean Ge(111) reconstruction, (b) Ag-induced structures, and (c) Li-induced structures.

structure of the clean Si(111) surface are almost identical with those of Ag on Si(111). This behavior may also apply to the Ge(111) surface. The $(\sqrt{3}\times\sqrt{3})$ structure of silver on Ge(111) has been observed by a number of groups.[8,9] We compare it here to the clean Ge(111) $(\sqrt{3}\times\sqrt{3})$ structure and the Li-on-Ge(111) $(\sqrt{3}\times\sqrt{3})$ structure.

Figure 5 shows the *I-V* curves of the three $(\sqrt{3}\times\sqrt{3})$ structures observed for the Ge(111) surface: clean surface, Ag exposed, and Li exposed. The *I-V* curves for the clean-surface reconstruction have a smaller total-energy range and are less smooth, especially at $E > 100$ eV, than those of the Ag- and Li-induced structures. This is a result of high background in the diffraction pattern, an indication of nonideal surface order as a result of the short-time anneal. Comparison of the sets of *I-V* curves in Fig. 5 clearly indicates the similarities between the curves. In the low-energy region ($E < 100$ eV), the *I-V* curves of the clean-surface structure are very similar to those of Ag on the Ge(111) surface. In the higher-energy region ($E > 100$ eV), the curves for Ag and Li on the Ge(111) surface are quite similar to each other. However, the *I-V* curves for Li on Ge(111) at $E < 100$ eV are less similar to the other two.

The similarities of the *I-V* curves in Fig. 5 are not surprising, as similar results have been reported for the Si(111) system.[6,10] The $(\sqrt{3}\times\sqrt{3})$ structures observed under Ag and Li adsorption are, therefore, probably due to the same surface reconstruction responsible for the clean Ge(111) $(\sqrt{3}\times\sqrt{3})R\,30°$ structure. The adsorbates form no long-range-ordered structures, but partially diffuse into the surface and stabilize the $(\sqrt{3}\times\sqrt{3})$ surface reconstruction. The difference in the *I-V* curves for Li on the Ge(111) surface at $E < 100$ eV possibly results from a significant change of the electronic potential barrier within the first several atomic layers as a result of alkali-metal adsorption. It is also interesting to note here that Na and K *do not* induce the $(\sqrt{3}\times\sqrt{3})$ structure over the exposure and temperature ranges studied here.

## IV. CONCLUSIONS

A $(\sqrt{3}\times\sqrt{3})R\,30°$ reconstruction of the clean Ge(111) surface has been observed. The same $(\sqrt{3}\times\sqrt{3})$ reconstruction is also observed upon Ag and Li adsorption and anneal. A $(1\times3)$ reconstruction of the Ge(111) surface has been also induced by alkali-metal adsorption. The Li, Na, and K adsorbates have no long-range-ordered structures in the $(1\times3)$ reconstruction. At K exposure of $>0.4$ ML, a $(2\times2)$ structure and a $(2\sqrt{3}\times2\sqrt{3})R\,30°$ structure is observed on the Ge(111) surface.

## ACKNOWLEDGMENTS

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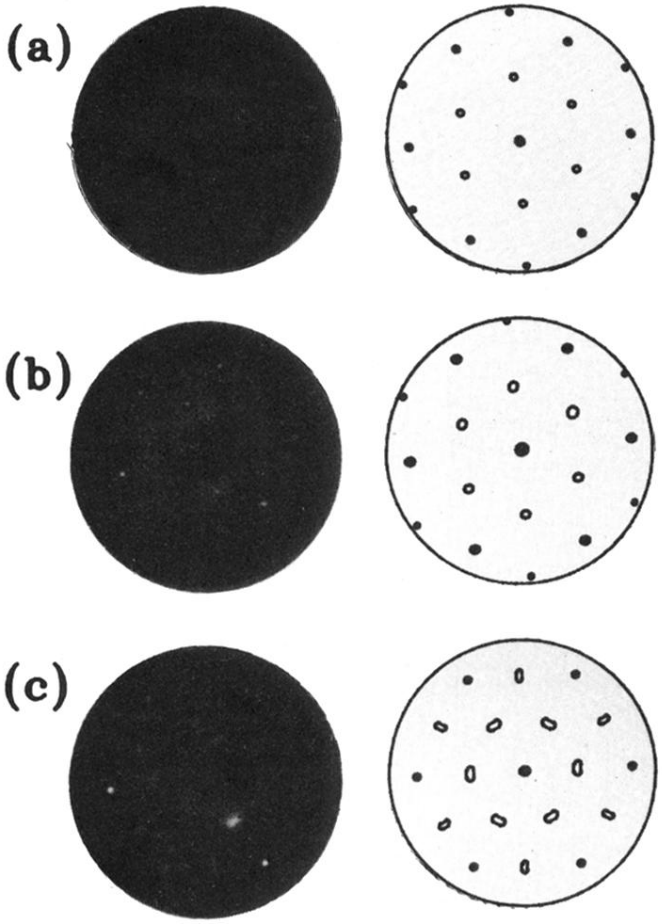

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